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(54) Title: PROCESS FOR PRODUCING A PURIFIED LACTIC ACID SOLUTION

(57) Abstract: The present disclosure provides a process for preparing a purified lactic acid solution suitable for use in connection with a source of lactate material a pH within the range of 0.8 to 9.0. The process includes the steps of providing a source of lactate material which includes a calcium salt; acidulating the concentrated broth with sulfuric acid to form an acidulated solution which includes lactic acid and calcium sulfate; reducing an amount of calcium sulfate from the acidulated solution; extracting the acidulated solution with an amine extractant to form a loaded solvent; and back extracting the loaded solvent with an aqueous solvent to provide a purified solution of lactic acid. Optionally, the source of lactate material can be concentrated prior to the step of acidulating. Alternately, the amine extractant can include sulfate anion. The sulfuric anion in the amine extractant can be residual sulfuric acid from the acidulation step. Alternately, the sulfuric acid in the amine extractant can be added during the extraction step, for example, as sulfuric acid.

PROCESS FOR PRODUCING A PURIFIED LACTIC ACID SOLUTION

FIELD OF THE INVENTION

The present invention relates to lactic acid processing. It particularly concerns a method for obtaining a purified lactic acid solution from a source of lactate material having either a neutral or low pH, and the resulting products.

BACKGROUND

The potential of lactic acid as a commodity chemical, for example for use in the production of various industrial polymers, is known. The use of lactic acid as a commodity chemical is particularly of interest because polylactic acid and many of its products are biodegradable. Additionally, lactic acid can be produced by fermentation, using renewable carbon sources.

Low pH fermentation is a process under investigation for improving the commercial viability of lactic acid production. In contrast to neutral pH fermentation (e.g., pH in the range of 5.0 to 8.0, inclusive, more typically 5.0 to 7.0, inclusive) in which the lactate material is mainly present as a lactate salt, lactate material formed using a low pH fermentation (e.g., at a pH below 5.0, typically below 4.8, more typically below 4.3) includes a significant amount of the free acid form. Thus, isolating lactic acid from an aqueous solution having a pH below 5.0 tends to reduce the need for acidulation technology typically necessary for isolating lactic acid from an aqueous solution having a pH above 5.0.

Many acidification technologies have significant capital costs or operating costs; consume acidification reagents; and/or result in the consumption of reagents and formation of by-product salts. Therefore, there is an interest in developing organisms that are capable of retaining high productivity at pH ranges of 5.0 or lower.

In addition to the effort to develop organisms having high productivities at a low pH, there is an effort to increase the use of mixed sugar streams during fermentation. Unlike traditional fermentation media, which typically includes a purified sugar stream such as dextrose as a carbon source, mixed sugar streams include combinations of hexoses, hexuloses, and pentoses such as dextrose, galactose, fructose, arabinose, and xylose. Mixed sugar streams are a lower cost

carbon source that can be obtained, for example, by enzymatic or acid hydrolysis of cellulose and hemicellulose. U.S. Patent Nos. 5,562,777, 5,620,877 and 4,350,766 discuss methods for making mixed sugar streams. U.S. Patent Nos. 5,798,237 and 5,789,210 discuss use of these streams as a carbon source for fermentation. The disclosure of these five patents are incorporated by reference herein.

Although mixed sugar streams provide a relatively low cost carbon source, mixed sugar streams typically have more impurities, such as lignin, than conventional dextrose streams. Not only do the impurities increase the burden on the microorganism, which must tolerate the impurities, the impurities also must be separated from the fermentation broth and the lactate material. Therefore, a separation process that is capable of reducing the presence of impurities due to the use of mixed sugar streams, or other carbohydrates sources, is also desirable.

SUMMARY

The present disclosure provides a process for preparing a purified lactic acid solution suitable for use in connection with a source of lactate material having either a neutral pH (e.g., between about 5.0 and 8.0, inclusive, more typically between about 5.0 and 7.0, inclusive) or a low pH (e.g., below 5.0, typically below 4.8, more typically below 4.3).

One preferred process disclosed herein includes steps of providing a source of lactate material which includes calcium lactate; concentrating the source of lactate material to form a concentrated solution; acidulating the concentrated solution with sulfuric acid to form an acidulated solution which includes lactic acid and calcium sulfate; reducing the amount the calcium sulfate in the acidulated solution; extracting the acidulated solution with an extractant to form a loaded solvent; and stripping the loaded solvent to provide a purified solution of lactic acid, for example, by back extraction with an immiscible aqueous solution. The process steps do not have to be performed in the order recited. For example, the step of concentrating can be performed before and/or after the step of acidulating.

Alternately, the process can be applied in a manner including the steps of providing a source of lactate material which includes calcium lactate; acidulating the source of lactate material with sulfuric acid to form an acidulated solution which

includes lactic acid and calcium sulfate; reducing the amount of calcium sulfate in the acidulated solution; combining the acidulated solution with an extractant to form an extraction solution wherein the extraction solution includes sulfuric acid, extracting the acidulated solution with the extraction solution to form a loaded solvent; and stripping the loaded solvent to provide a purified solution of lactic acid. The sulfuric acid in the extraction solution can be residual sulfuric acid from the acidulation step. Alternately, sulfuric acid can be added to the extraction solution prior to or during the extraction step.

Optionally, the process can be applied in a manner that includes a step of reducing the amount of impurities having a molecular weight of about 5,000 Da and greater in the source of lactate material prior to the step of concentrating. Preferably, the source of lactate material includes a fermentation broth and calcium lactate is formed a result of using calcium carbonate or calcium hydroxide as pH controlling agents during the fermentation.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a process flow chart showing a process for generating a purified lactic acid solution.

FIG. 2 is a process flow chart of an alternate process for generating a purified lactic acid solution.

FIG. 3 is a plot showing a McCabe-Thiele diagram for the extraction of lactic acid in an amine extractant.

FIG. 4 is a plot showing the equilibrium curves of an amine extractant with and without sulfate present in the extract.

DETAILED DESCRIPTION

The invention provides a process for obtaining a purified lactic acid solution from a source of lactate material having either a neutral or low pH. Typically, the source of lactate material includes a fermentation broth. As used herein, "fermentation" refers to any metabolic process that produces a useful product by the mass culture of microorganisms. A variety of microorganisms are suitable for use in the fermentation process, for example, bacteria, yeast and fungi. The term

WHAT IS CLAIMED IS:

1. A process for generating a purified solution of lactic acid, comprising the steps of:

(a) providing a source of lactate material which includes at least one of lactic acid, lactate salt, or both wherein the lactate salt includes calcium lactate;

(b) concentrating the source of lactate material by removing at least about 10% of the volume of the source of lactate material without similarly reducing the volume of lactate material to form a concentrated solution;

(c) acidulating the source of lactate material with sulfuric acid to form an acidulated slurry which includes lactic acid and calcium sulfate;

(d) removing at least some calcium sulfate from the acidulated slurry;

(e) extracting the acidulated solution with an amine extractant to form a loaded solvent; and

(f) stripping the loaded solvent to provide a purified solution of lactic acid.

2. The process of claim 1, wherein said step of stripping includes a step of back extracting the loaded solvent with an aqueous solvent.

3. The process of claim 1, wherein said amine extractant is combined with sulfuric acid prior to said step of extracting.

4. The process of claim 1, further comprising a step of adding sulfuric acid to the amine extractant during the step of extracting.

5. The process of claim 1, further comprising a step of reducing an amount of impurities having a molecular weight of about 5,000 to 500,000 Da in the source of lactate.

6. The process of claim 1, wherein the step of providing a source of lactate material includes providing a source of lactate material having a pH between about 5.0 to about 9.0.

7. The process of claim 1, wherein the source of lactate material has a pH below about 5.0.

8. The process of claim 1, wherein the source of lactate material is a fermentation broth.

9. The process of claim 8, wherein calcium carbonate or calcium hydroxide is included in the fermentation broth.

10. The process of claim 1, wherein mixed sugars are included as a carbon source in the fermentation broth.

11. The process of claim 1, wherein the amine extractant includes tertiary amines.

12. The process of claim 1, wherein the amine extractant includes less than 5wt% polar organic enhancer.

13. The process of claim 1, wherein the amine extractant includes sulfate within the range of about 0.01 mole/Kg to about 1.0 mole/Kg sulfate.

14. The process of claim 1, wherein the amine extractant includes Alamine 304 and IsoPar K.

15. The process of claim 1, further comprising a second step of concentrating the acidulated solution before said step of extracting.

16. The process of claim 15, further comprising a step of reducing an amount of residual calcium sulfate prior to said second step of concentrating the acidulated solution.

17. The process of claim 1, further comprising a step of extracting the loaded solvent with a minor amount of aqueous solution prior to said step of back extracting.

18. The process of claim 1, wherein said step of concentrating is performed prior to said step of acidulating.

19. The process of claim 1, wherein said step of acidulating is performed prior to said step of concentrating.

20. The process of claim 1, further comprising a step of converting the purified lactic acid to lactate esters or lactide.

21. A process for generating a purified solution of lactic acid, comprising the steps of:

(a) providing a source of lactate material which includes calcium lactate salt;

(b) acidulating the source of lactate material with sulfuric acid to form an acidulated slurry which includes lactic acid and calcium sulfate;

(c) removing at least some calcium sulfate from the acidulated slurry;

(d) combining the acidulated solution with an amine extractant to form an extraction solution wherein the extraction solution includes sulfuric acid,

(e) extracting the lactic acid from the acidulated solution with the amine extractant to form a loaded solvent; and

(f) back extracting the loaded solvent with an aqueous solvent to provide a purified solution of lactic acid.

22. The process of claim 21, wherein the sulfuric acid in the extraction solution derived from the residual sulfate in the lactic acid solution after gypsum filtration.

23. The process of claim 21, further comprising a step of adding sulfuric acid to the extraction solution.

INTERNATIONAL SEARCH REPORT

Information on patent family members

Inter. onal Application No
PCT/US 00/27200

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9815517 A	16-04-1998	AU 4891497 A	05-05-1998
		EP 0932592 A	04-08-1999
WO 9919290 A	22-04-1999	AU 1080199 A	03-05-1999
		BR 9814641 A	03-10-2000
		CN 1275973 T	06-12-2000
		EP 1023258 A	02-08-2000
		NO 20001765 A	14-06-2000

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Message:

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Attached are some of the pages from PCT WO01/25180.

Mike